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Chemical Structure of Char in the Transition from Devolatilization to Combustion

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Introduction

Recent coal devolatilization efforts have focused on relating coal devolatilization behavior to the chemical structure of the parent coal.[1-6] Gas and tar yields, as well as tar molecular weights, can be predicted based on correlations related to elemental compositions or from measured chemical characteristics of the parent coal. However, char is an important product produced during coal devolatilization, and must be characterized as a function of temperature and heating rate in a manner similar to volatile devolatilization products. Quantitative measurements of chemical structure are performed on the coals and chars using ^{13}C nuclear magnetic resonance (NMR) techniques described by Solum and coworkers.[7]

The chemical structures of char and tar during devolatilization for an Illinois #6 coal and a lignite were published previously, and discussed relative to devolatilization behavior.[8,9] These data showed that during the tar release period, the percentage of aromatic carbon for the bituminous coal char changed by less than 5%, while the carbon aromaticity in the lignite char changed in the early stage of pyrolysis. The carbon aromaticities for both sets of chars ultimately reached comparable values, but the parent lignite had a lower carbon aromaticity value ($f_a' = 0.57$) than the parent bituminous coal ($f_a' = 0.67$). The number of aromatic carbons per cluster indicated restructuring of the aromatic species earlier in the lignite than in the Illinois No. 6 coal.

In this work, the chemical structure of chars from five coals of different rank are examined, and implications on char reactivity are discussed. Chars were obtained as a function of residence time in two flow reactors generally used for devolatilization and char combustion experiments, respectively. The examination of five coals and their respective chars from two reactors allows better distinction of trends than was possible with the limited data previously published.

Experimental Approach

Char samples were collected as a function of residence time in an entrained flow, laminar reactor in the Sandia Coal Devolatilization Laboratory (CDL) in 100% nitrogen to isolate the pyrolysis reactions, with typical particle heating rates of 2×10^4 K/s, gas temperatures of 1250 K, and particle temperatures as high as 1200 K.[2,3] Additional char samples were collected in an entrained flow, laminar flow reactor in the Sandia Char Combustion Laboratory (CCL), with a laminar $CH_4/H_2/O_2/N_2$ flat flame providing a high temperature environment (maximum gas temperature = 1600 K).[10] Stoichiometric conditions were used in the flame, yielding less than 50 ppm O_2 in the post-flame gases. Char samples in the CCL were collected subsequent to the visible region of coal devolatilization, with particle heating rates of about 5×10^4 K/s and particle temperatures of

[*] Experiments performed at the Combustion Research Facility, Sandia National Laboratories, Livermore, CA.

approximately 1300 to 1500 K, depending on residence time and oxygen concentration.[10] Common coal samples were used in the coal devolatilization and char oxidation experiments discussed here.

Helium-quench probes were used to collect char samples,[2,10] and chars were analyzed for organic and inorganic elemental composition. The experiments in the CCL with no post-flame oxygen required modifications to the sampling system to aerodynamically separate tars, soot and aerosols from char particles. The extent of mass release from the char particles was determined from the trace mineral species (Si, Al, Ti, and total ash). Samples were obtained in the CDL at different residence times in the 1250 K gas condition, with residence times ranging from 20 to 250 ms. Samples were taken just subsequent to the pyrolysis zone (47 ms, 6.4 cm above the burner) in the CCL.

Results

The elemental compositions of the five coals used in these experiments are shown in Table 1, along with their total volatiles yields in the two reactors. The coals range in rank from a lignite to a low-volatile bituminous coal. The volatiles yields in the CCL are slightly higher than those in the CDL, and are much higher than the ASTM analyses.[11] Results of the ^{13}C NMR chemical structure analyses of CDL chars are presented first, followed by data for the CCL chars.

Table 1
Elemental Analyses of Coals Used

PSOC-	Coal	Size Fraction (μm)	C (% daf)	H (% daf)	O (% daf)	N (% daf)	S (% daf)	Ash (% dry)	CDL Volatiles Yield (% daf)	CCL Volatiles Yield (% daf)
1507D	Beulah Zap (lignite)	75-106	66.56	4.26	25.16	1.12	2.89	18.7	53.7	58.6
1445D	New Mexico Blue (subbituminous)	106-125	75.6	5.26	17.33	1.32	0.49	3.48	53.4	56.2
1493D	Illinois No. 6 (hvb bituminous)	106-125	74.12	4.96	13.18	1.45	6.29	11.30	53.5	58.3
1451D	Pittsburgh No. 8 (hva bituminous)	63-75	84.23	5.54	7.56	1.65	1.01	3.73	53.1	52.2
1508D	WV Pocahontas (lv bituminous)	106-125	88.83	4.37	5.14	1.06	0.6	16.72	15.9	17.4

A. Chemical Structure of Coal Chars from the CDL

Attachments per Cluster. Attachments to aromatic clusters consist of alkyl groups and oxygen functional groups (e.g., phenols and/or alkyl and aryl ethers). These attachments are either bridges and loops between aromatic clusters or side chains. The bond strengths of the aromatic rings are much greater than the bond strengths of the labile bridges and loops. During devolatilization the labile bridges break, generating finite-size fragments containing one or more aromatic clusters. The light fragments are released as tar, while the heavier fragments stay in the char as metaplast and eventually reattach to the infinite char matrix. Broken bridge fragments (i.e., side chains)[1] are eventually released as light gas. In this analysis, it is assumed that the broken bridge fragments may be distinguished from intact bridges by the presence of methyl groups. Hence, the number of side chains per cluster can be estimated together with the number of intact bridges and loops per cluster. It is important to note that aliphatic carbons still remain at the end of the pyrolysis process and represent the presence of stable aliphatic bridge material and/or side chains that have not been expelled at the pyrolysis temperatures employed.

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The total number of attachments per cluster (referred to as the coordination number, $\sigma+1$) is shown in Fig. 1 for char samples from all five coals. The coordination number either remains relatively constant or decreases slightly during devolatilization for all five coals. This means that no new attachment sites are generated during pyrolysis; any reattachment of metaplast occurs at existing side chain sites. Decreases in the coordination number can be explained by the release of side chains with no subsequent crosslinking at that site.
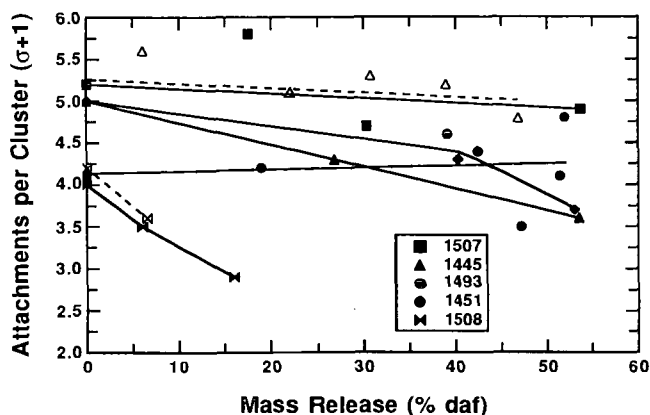

Figure 1.   The total number of attachments per cluster vs. the extent of mass release due to devolatilization for chars collected at different residence times in the 1050 K (dashed lines and open symbols) and 1250 K (solid lines and filled symbols) gas temperature conditions.

The number of bridges and loops (i.e., bridges between aromatic rings and aliphatic loops on aromatic rings, such as tetralin) per cluster does not change significantly in the Illinois #6 coal char until the end of the mass release period, as shown in Fig. 2. The increase in the number of bridges and loops per cluster is an indication of the extent of crosslinking that occurs between neighboring aromatic clusters. The total number of attachments per aromatic cluster ($\sigma+1$), however, does not change significantly, indicating that bridge material is released at a rate proportional to the formation of crosslinking bridges. These stable char bridges likely are formed at the site of the original bridge. These data at rapid heating conditions clearly indicate that the average molecular structure of the Illinois No. 6 coal does not undergo major changes in functional group distribution until after most of the tar is released, at which time reactions occur in the char/metaplast that are associated with gas release.

The crosslinking behaviors of the chars from other coals, as indicated by the NMR data, are different from that observed in Illinois No. 6. The changes in the number of bridges and loops per cluster in the late stages of mass release for the other bituminous coal (PSOC-1451) are more scattered, and do not exhibit the clear indication of crosslinking observed in the Illinois #6 coal (PSOC-1493). In the lignite, the initial number of bridges and loops is slightly higher than in the bituminous coals, and increases in a monotonic progression with the extent of mass release, as reported earlier.[9] The lignite data reflect the early crosslinking that is observed in solvent swelling measurements of lignites as compared to the high volatile bituminous coals.[12,13] This early crosslinking is only indicated in Fig. 2 for the lignite; none of the other coals show significant increases in the number of bridges and loops

per cluster until the late stages of mass release (including the subbituminous coal). The highest rank coal (PSOC-1508 Pocahontas lv bituminous) shows a slight decrease in the number of bridges and loops per cluster as mass release proceeds.
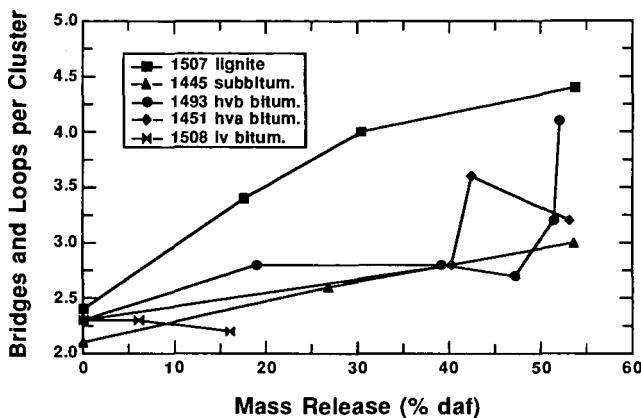

Figure 2.   The number of bridges and loops per cluster vs. the extent of mass release due to devolatilization for chars collected at different residence times in the 1250 K gas temperature condition.

Coordination numbers for char samples obtained in the 1050 K gas condition in the CDL are shown as dashed lines and open symbols in Fig. 2. In the 1050 K gas condition, the coordination number determined for the chars from the subbituminous coal (PSOC-1445) does not decrease as much with mass release as indicated at 1250 K. The lower temperature condition does not permit the same degree of gas release as the higher temperature condition, and hence more side chains remain attached to the clusters. The coordination number data at 1050 K for the high rank coal (PSOC-1508) follow the data indicated at 1250 K. In general, the data at 1050 K support the conclusion inferred from the 1250 K data; no increases in the number of attachments per cluster are seen, indicating that crosslinking occurs only at existing side chain sites.

Carbon Aromaticity. The carbon aromaticities of the fully-devolatilized chars only range from 79% for the subbituminous coal to 88% for the Pittsburgh No. 8 and the Pocahontas coals, whereas $f_a{}'$ in the parent coals range from 53% for the subbituminous coal to 77% for the Pocahontas coal. The carbon aromaticity measured for the subbituminous coal and char is uniformly lower than measured in the other four coals (and their chars). The carbon aromaticities of the fully-devolatilized chars from the other four coals lie in a narrow range from 84% to 88%.

Cluster and Attachment Molecular Weights. The average cluster molecular weight determined from the NMR analyses includes the aromatic carbons per cluster plus the attachments (bridges and side chains) to the cluster, i.e., the contributions from both the aromatic and aliphatic material in the vicinity of a cluster. Cluster molecular weights of chars collected in the CDL at the 1250 K gas condition as a function of residence time are shown in Fig. 3. The average cluster molecular weight for parent coals ranges from 270 amu for the Illinois No. 6 coal to 440 amu for the Zap lignite, as shown in Fig. 3 at a

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residence time of 0 ms. However, as these coals are heated and the volatiles are released, average cluster molecular weights for the chars of these different coals become very similar.
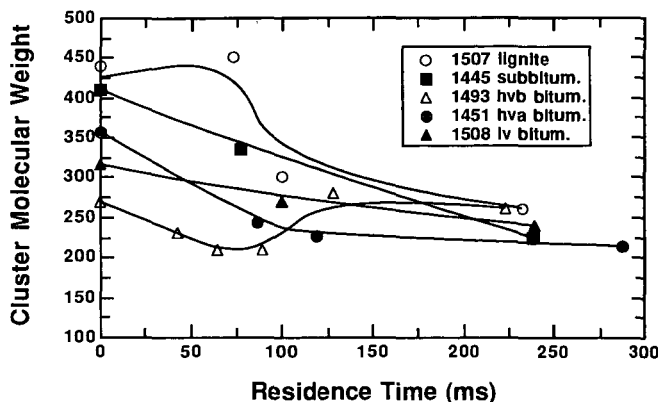

Figure 3.   Average cluster molecular weights in coals and chars collected in the 1250 K gas condition in the CDL, determined from ^{13}C NMR analyses. Parent coals are represented at 0 ms residence time.

Another comparison of chemical structure as a function of coal rank is the average molecular weight of attachments to clusters in the parent coal. Attachments to clusters include labile bridges ($\pounds$), char bridges (c), and side chains (δ). The molecular weight of attachments m_{att} can be calculated from the cluster molecular weight by subtracting the mass in the aromatic fused structure (the number of aromatic carbons per cluster multiplied by the molecular weight of carbon) and dividing by the number of attachments per cluster:

$$m_{att} = \frac{M_{clust} - C_{clust} M_C}{\sigma + 1} \tag{1}$$

The definition of the molecular weight per cluster (M_{clust}) used here includes the mass in the aromatic part of the cluster plus the surrounding aliphatic material. The cluster molecular weight therefore includes the mass of side chains, and one-half the molecular weights of labile bridges and char bridges attached to the cluster, as follows:

$$m_{att} = \frac{\pounds \frac{m_b}{2} + c \frac{m_{char}}{2} + \delta \, m_\delta}{\pounds + c + \delta} \tag{2}$$

where $\pounds, c$, and δ represent the populations of labile bridges, char bridges, and side chains, respectively. The factor of 2 in the m_b and m_c terms reflects the fact the only one-half of an intact bridge is attributed to a cluster. Unreacted coals contain very few char bridges (i.e., $c = 0$), and hence Eq. 2 reduces to the relation $m_{att} = m_\delta$ assuming that $m_\delta = m_b/2$. For fully-devolatilized chars, $\pounds = 0$.

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Attachment molecular weights have been thus determined for all five coals examined in the Sandia devolatilization experiments, as well as for chars at different residence times, as shown in Fig. 4. Attachment molecular weights for other parent coals are also shown, as reported by Solum, et al.[7] for the Argonne premium coals[14] and for three coals examined at Advanced Fuel Research (AFR).[15] The continuous lines in this figure represent linear correlations of the data. The oxygen content of the parent coal is an indicator of coal rank; the oxygen content of the parent coal decreases as coal rank increases. The attachment molecular weights of the parent coals exhibit a definite trend as a function of coal rank; values of m_{att} range from 52 amu in the lignite and subbituminous coal (25% daf oxygen) to 13 amu for the highest rank coal (Pocahontas #3 lv bituminous, Argonne sample).
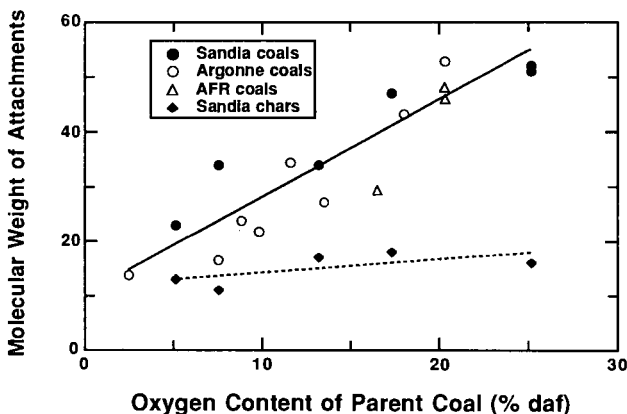

Figure 4.   Average molecular weight of attachments to aromatic clusters in unreacted and fully-devolatilized coals as a function of coal type. Data for non-Sandia coals are taken from Solum, et al.[7]. Fully-devolatilized chars are from the longest residence time (~ 250 ms) in the 1250 K gas condition in the CDL.

The fully-devolatilized chars in Fig. 5 are from the longest residence time (~ 250 ms) in the 1250 K gas condition in the CDL (in 100% N_2). The molecular weights of attachments for the fully-devolatilized chars vary from 18 to 11 amu, which is not a significant dependence on coal rank. The fully-devolatilized chars do not contain any labile bridges, and hence the attachments to the cluster consist solely of char bridges and side chains. The fact that the average molecular weight of attachments to aromatic clusters in the fully-devolatilized chars is low enough (11 to 18 amu) to compare with bridges consisting of one atom (12 amu for carbon, 16 amu for oxygen) suggests that low molecular weight side chains may consist mainly of methyl groups (15 amu) and OH groups (17 amu), which are more stable than longer side chains such as COOH or ethyl groups (C_2H_5).

Stable char bridges are thought to mainly consist of three types: (a) biphenyl bridges, where a bridge is formed between neighboring carbons on different aromatic clusters (Ar-Ar); (b) ether-type bridges where a single oxygen atom forms a bridge between neighboring clusters (Ar-O-Ar); and (c) a carbon bridge, thought to mainly consist of single carbon atoms between clusters (Ar-C-Ar). The molecular weights of these three types of bridges are low enough to be consistent with the NMR data: 0 amu for the biphenyl bridge; 16 amu for the oxygen bridge; and 14 amu for the carbon bridge.

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Discussion of CDL Data. It is well known that the physical structures (i.e., apparent densities and internal surface areas) of these chars vary significantly, causing a difference in the *apparent* reactivities of these chars (based on external surface area). However, the similarity in chemical structure of the fully-devolatilized chars from different coals may imply that the *intrinsic* chemical reactivities of these chars may be similar. The exact relationship between cluster molecular weight, carbon aromaticity, and intrinsic chemical reactivity is not yet clear. The fact that the chemical structure of these chars are similar is somewhat surprising because the chemical compositions of these chars are different. The carbon contents of the fully-devolatilized chars vary from 83% on a dry ash-free (daf) basis for the lignite char to 92% daf for the Pocahontas char. The oxygen contents of these chars range from 9.9% daf for the lignite char to 3.3% daf for the Pocahontas char. The NMR chemical structure data on chars should be compared in the future with physical structure and reactivity data.

B. Chemical Structure of Coal Chars in the CCL

Char samples from five coals collected at 47 ms residence time in the CCL with 0% post-flame oxygen were analyzed by ^{13}C NMR spectroscopy. The chars taken from the CCL-0 condition are very similar in chemical structure to the chars taken immediately after tar release in the CDL experiments at 1250 K (residence times of approximately 70 to 100 ms). In the CDL, these chars have finished releasing tar, and are beginning the slower gas release phase. The chars in the CCL-0 condition at 47 ms have just completed tar release as well, and hence should be followed by a slower light gas release region. The similarity in chemical structure of chars from the 1250 K gas condition in the CDL and from the CCL-0 condition is shown in Fig. 5. The solid lines in these figures represent the CDL data at different residence times, while the dashed line represents data from the CCL-0 experiments. Residence time for a given coal is in the vertically upward direction.
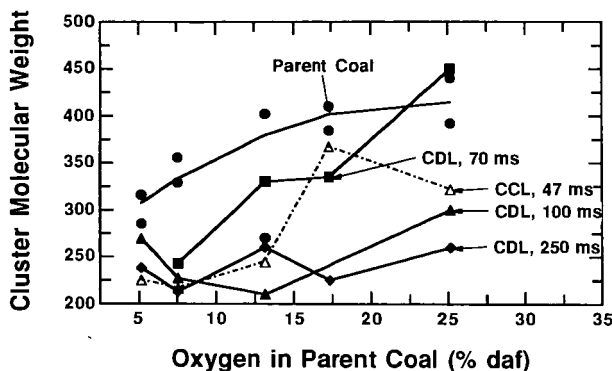

Figure 5.   Comparison of cluster molecular weights in char samples from the CCL-0 condition and the 1250 K gas condition in the CDL (see caption to Fig. 6).

The cluster molecular weights (Fig. 5) in the CCL-0 chars from the low rank coals generally lie between the values observed in the chars collected at 70 and 100 ms in the CDL. In contrast, the cluster molecular weights in CCL-0 chars from the high rank coals are most similar to the CDL chars collected at 100 ms. Similar trends were observed in the carbon aromaticities of the chars from the CDL and CCL.

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Quantitative measures of chemical structure (e.g., carbon aromaticities, cluster molecular weights) for the CCL-0 chars always lie close to the values observed in the chars collected at 70 or 100 ms in the CDL, and do not approach the values observed at 250 ms in the CDL. The chemical structure data for the CCL-0 chars therefore indicate that tar release in the CCL is complete at 47 ms, but that further release of light pyrolysis gases is still underway in the early stages of char combustion. Simultaneous char combustion and light gas evolution occur as the char ignites, and both must be considered in the determination of reactivities early in the char combustion process.

Conclusions

The chemical structures of chars from an electrically-heated laminar flow reactor (CDL) and a flame-driven flow reactor (CCL) show remarkable similarities. The CCL chars are similar to the chars that were collected in the CDL immediately after tar release, but before the further release of light gases. This indicates that char combustion occurs concurrently with the late degassing stage of devolatilization. The fully-devolatilized chars from the CDL exhibit similar chemical structure characteristics, such as molecular weight per cluster and attachment molecular weight, even though the parent coal structures are quite different. The similarity in chemical structure of the chars is in contrast to the general trend in char reactivity (in oxygen); low rank coals are generally more reactive than high rank coal chars. This implies that the principal cause of differences in char reactivity is physical structure (e.g., internal surface area, porosity) rather than chemical structure.

Acknowledgements

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